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Thin films of Eu-doped GaN are irradiated with 500 keV He^+ ions to understand radiation damage mechanisms and to quantify luminescence efficiency. Ion beam induced luminescence was monitored spectroscopically as function of fluence. Behavior observed is consistent with simultaneous creation of non-radiative defects and destruction of luminescent centers associated with the 4*f*-4*f* core-level transition in Eu^{3+}. This model contrasts with a previous description which takes into account only non-radiative defect generation in GaN:Eu. Based on light from a BaF_2 scintillator standard, the luminescent energy generation efficiency of GaN:Eu films doped to ~3×10^{18} cm^{-3} Eu is estimated to be ~0.1%.

Eu-doped GaN is a promising material for optoelectronic devices, having demonstrated efficient conversion of energetic electrons to light.[1-11] The triply-ionized Eu atom, situated in the Ga position of the GaN lattice, exhibits strong photo-luminescence at ~621 nm (~2 eV) due to the 4*f*-4*f* core-level transition $^5D_0$-$^7F_2$. This wavelength is technologically important because it facilitates fabrication of monolithic GaN-based devices composed of diodes emitting light at red, green and blue wavelengths.[12] Further, Eu-doped GaN films show potential for operation in radiation environments, since luminescence remains relatively constant even after exposure to high fluences of 3 MeV electrons. It is has been hypothesized that traps introduced in the GaN matrix during irradiation have little effect on the Eu-related luminescence because the distance between nearest neighbor Eu atoms can be made small relative to the minority carrier diffusion length in GaN. Excited electrons are therefore captured by the Eu centers and their energy converted to light before they can non-radiatively recombine with holes in GaN.[13]

Here we use *in-situ* optical measurements to examine the mechanisms for light emission and damage in Eu-doped GaN thin films. We show that the luminescence due to the Eu ion can be quenched by moderate fluences of energetic He^+ ions, thereby demonstrating the ultimate limits of radiation tolerance in this material. We quantitatively explain the origin of the damage by introducing a new model that takes into account both the creation of nonradiative traps and the destruction of Eu^{3+} luminescent centers. Finally, we estimate the efficiency of the ion-beam induced luminescence process by making use of a scintillator, BaF_2.

Undoped, <0001>-orientated GaN films, synthesized by Cree, Inc., on sapphire, were implanted to ~5×10^{14} cm^{-2} with Eu ions at 190 keV, 5° tilt relative to the wafer normal. Films were ~2.4 μm thick, n-type, with electron carrier concentration less than 10^{16} cm^{-3}. Implanted wafers were diced into 1 cm^2 pieces, then annealed to activate the Eu atoms with pieces positioned front-to-front in a N_2 ambient at 1025 °C for 90 minutes. Subsequently, secondary ion mass spectrometry (SIMS) measurements were performed to establish the concentration of active Eu atoms in the film.[14] SIMS showed that some N had evaporated during annealing, but that a concentration of ~1.5×10^{-2} atomic percent Eu remained in stoichiometric GaN at a depth of 0.4 μm, tailing off noise levels below 5×10^{-5} atomic percent at a depth of 1 μm. Between depths of 0.4 and 1 microns, the average concentration of active Eu atoms is 3×10^{-3} atomic percent.

Activated GaN:Eu films were exposed to 500 keV He^+ in the LLNL 4 MeV Ion Beam Accelerator. Films were oriented at 45° to the incoming beam during irradiation, and masked with a stainless steel shield such that the area exposed was 7.1×10^{-2} cm^2. Dose rates on this area were between 6.9×10^9 and 1.4×10^{12} ions/sec/cm^2. Light from He^+ ions incident on GaN:Eu was collected *in situ* during irradiation with a 5 mm diameter collimating lens mounted 1.8 cm from the sample and fiber. The light was then spectoscopically analyzed and recorded with a cooled spectrometer. Photoluminescence measurements were also performed on the films before and after irradiation using a 395 nm excitation source operating at 4 W/cm^2. With SRIM 2003, we estimate the range of 500 keV He^+ ions, incident at 45 ° to the GaN surface normal, to be ~0.9 μm.[15]

After exposure to a sufficient fluence of He^+ ions, photo-luminescence is quenched. Fig. 1 shows the photo-luminescence spectrum of the GaN:Eu obtained with laser excitation, before and after irradiation with 500 keV He^+ to dose of 5.3×10^{14} cm^{-2}. For comparison, the spectrum of He^+-excited light is shown in for 500 keV He^+ with a dose rate of 6.9×10^9 ions/s/cm^2. The spectrum generated by He^+ ions incident on GaN:Eu is very similar to the PL-generated spectrum, indicating that the same 4*f*-4*f* core-level transition in Eu^{3+}, $^5D_0$-$^7F_2$,[11] is responsible for the observed light in both cases. Differences in peak widths are attributed to differences in light collection optics between photoluminescence and alpha-induced measurement systems. For the measurement of alpha-induced luminescence, large diameter optical fibers were used to maximize light collection efficiency out of the vacuum chamber and into the spectrometer.

The peak intensity associated with the $^5D_0$-$^7F_2$ transition in Eu^{3+} decreases following exposure to 500 keV He^+ ions. Fig. 2 shows the normalized peak (~621 nm) ion-beam induced luminescence intensity as a function of fluence. Dose rates range between 5.5×10^{10} and 1.4×10^{12} ions/sec/cm^2. Note that the luminescence decay rate is not a strong function of the dose rate over this range. Model results are shown also, as will be discussed.

To understand the photoluminescence decay due to damage from 3 MeV electrons, the density of traps was previously assumed by Nakanishi et al. to be equal to radiation fluence, Φ, scaled by the trap production rate, K_t.[13]

$$N = K_t \Phi \quad (1)$$

We note that this is a strong assumption, but one which was successful for these electron experiments. The trap production rate was calculated to be ~7 cm^{-1}, with a constant radiative recombination lifetime, τ_r, of 1 ns, a thermal velocity, v_{th}, of 10^7 cm/s, and capture cross section for non-radiative traps, σ, of 10^{-15} cm^{-2} (0.1 nm^2).[13]

For ion-beam induced luminescence, we assume that the previous analysis developed for photoluminescence remains valid. This is supported by the fact that the emission spectra for the two processes are similar, as shown in Fig. 1. However, we find that the observed decay of luminescence as a function of ion fluence cannot be accounted for by trap production alone. For example, assuming constant τ_r, the best fit to He^+ luminescence data is shown as a dashed line in Fig. 2. Significant differences between the measured and modeled data are evident at both low and high fluences.

To explain the observed differences between measured and modeled data for ion beam-induced damage, we first assume that lifetime for radiative recombination, τ_r, can be described with:

$$\tau_r = \frac{1}{\sigma v_{th} N_r} \quad (2)$$

where N_r is the number of radiative recombination centers per unit volume (cm^{-3}), σ, the capture cross section, and v_{th}, is the thermal velocity of carriers. These centers are destroyed by the ion fluence, Φ, at a rate which is proportional to the number of remaining centers:

$$\frac{dN_r}{d\Phi} \propto -N_r \tag{3}$$

such that the number of radiative centers as a function of fluence is given by:

$$N_r = N_r^0 e^{-\alpha\Phi} \tag{4}$$

where α is the cross section for the destruction of radiative centers and N_r^0 is the initial concentration of radiative centers. We assume that the initial concentration of radiative centers is equal to the concentration of active Eu at depths between 0.4 and 1 μm in the GaN:Eu which is 3×10^{-3} atomic percent, or 2.6×10^{18} cm^{-3}. With this new model, we find that the trap production rate for 500 keV He^+ ions is ~5000 cm^{-1}, and that the cross section for radiative center destruction is 5×10^{-15} cm^{-2} (0.5 nm^2). The best fit of the new model to the data is shown in Fig. 2. Statistically comparing the old model with the new model using an F test, we calculate less than a 0.01% chance that the old model is a better fit for the data. Note that neither model fits well to the data at low fluences, suggesting that the rate of non-radiative defect generation may not be constant in this range, as assumed in (1) Note that if radiation tolerance is a function of the distance between

nearest neighbor Eu atoms as previously hypothesized[13], then thin films of GaN:Eu with higher Eu content may prove to be more immune to ion beam damage.

Finally, to estimate the absolute light emission efficiency of the GaN:Eu scintillator, we use BaF_2, an established scintillator with known alpha-to-photon conversion of 720 photons/MeV.[16] GaN:Eu generates approximately 1/3 of the total number of spectrometer counts vs. the GaN:Eu, implying a alpha-to-photon conversion of 240 photons/MeV. However, it is necessary to account for the fact that only a fraction of the total ion energy is deposited in the GaN volume which contains active Eu. The BaF_2 scintillator is a thick, homogenous slab which absorbs 100% of the He^+ energy. The active Eu, by contrast, is concentrated in a relatively thin band in the GaN as previously described. Using SRIM 2003[15] to calculate the energy deposition as a function of depth, and the SIMS measurement of active Eu content, we calculate that about 1/3 of the total ion energy is deposited in the GaN volume which contains active Eu. Therefore, the alpha-to-photon conversion 240 photoelectrons/MeV must be adjusted upward by a factor of three to 720 photoelectrons/MeV. Since each photon has ~2 eV (621 nm peak, see Fig. 1), the conversion efficiency of 0.003% active Eu in GaN is $2\times720/10^6$ = ~0.1 %, assuming the conversion rate is not dependent on the incident alpha particle energy.

In summary, ion-induced radiation damage in luminescent GaN:Eu thin films has been found to be associated with both the creation of defects and the destruction of luminescent centers. For 500 keV He^+ ions the trap production rate is ~5000 cm^{-1}, and the cross section for radiative center destruction is 5×10^{-15} cm^{-2} (0.5 nm^2). These values

may be compared to the trap production rate of 7 cm^{-1}, and the cross section for generation of non-radiative traps of 0.1 nm^2, previously measured for 3 MeV electrons.[13] As expected, the much heavier ions are more efficient at reducing luminescence intensity. Lightly Eu-doped (2.6×10^{18} cm^{-3}) GaN films are found to convert radiation energy to light with ~0.1 % efficiency. Increasing Eu content will likely improve this conversion efficiency[17-19] and may simultaneously improve radiation tolerance.

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Figure Captions

Fig. 1 Photoluminescence before and after irradiation of GaN:Eu with 500 keV He^+ ions to dose of 5.3×10^{14} cm^{-2}, shown with luminescence measured *in-situ* during irradiation of GaN:Eu with 500 keV He^+ ions at 6.9×10^9 ions/s/cm^2. Differences in peak width are due to differences in light collection optics between photoluminescence and alpha-induced luminescence measurement systems.

Fig. 2. Peak (~620 nm) ion-induced luminescence of GaN:Eu under irradiation by He^+, plotted as a function of fluence. Dose rates were 5.5×10^{10}, 2.8×10^{11} and 1.4×10^{12} ions/sec/cm^2. Results are shown for constant radiative recombination lifetime model, and for the new model wherein the radiative lifetime is exponentially dependent on the fluence. At fluences lower than ~2×10^{13} cm^2 where model agreement is lowest, the rate of non-radiative defect generation may not be constant.

Fig. 1

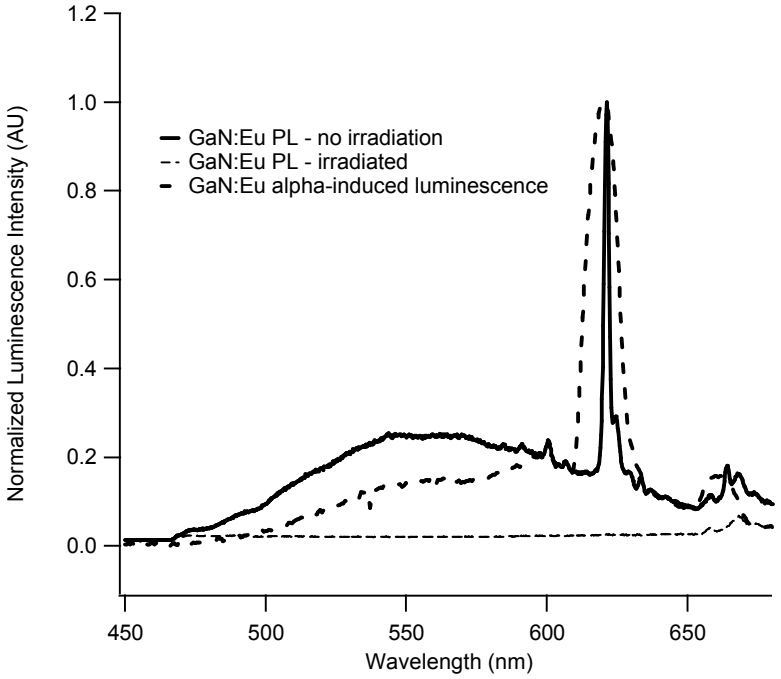
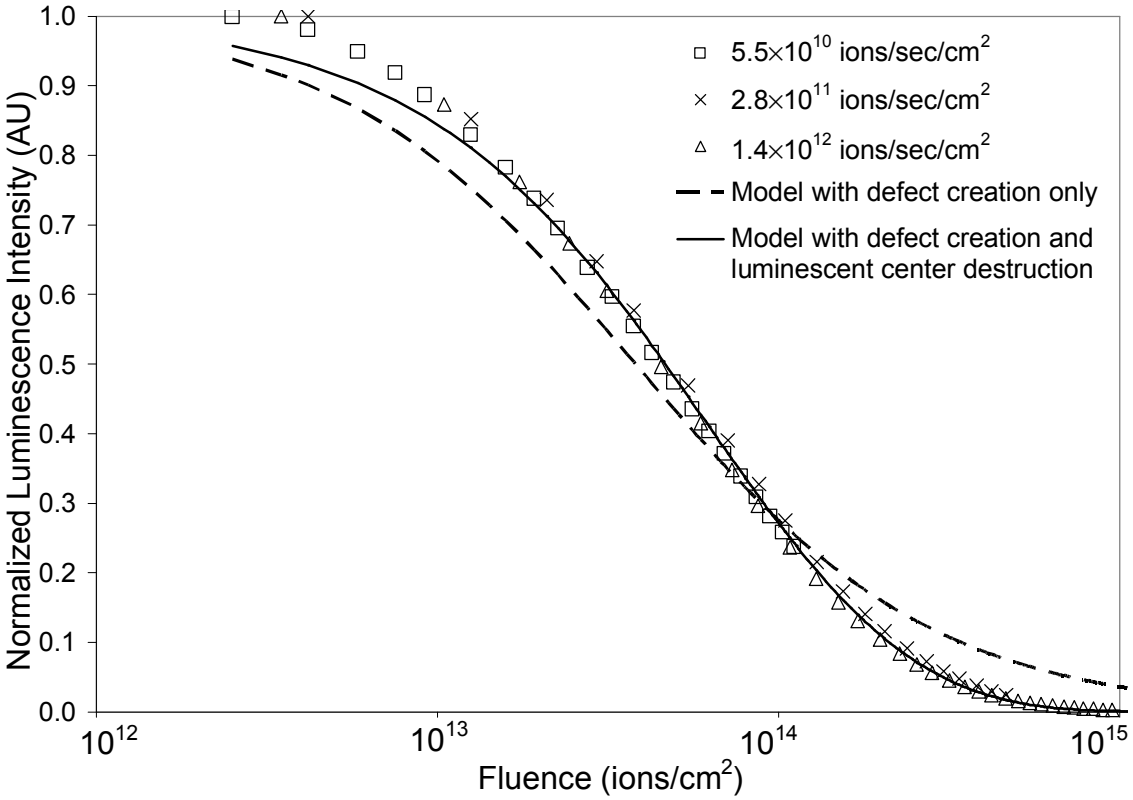

1.2
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Luminescence Intensity (AU)
GaN:Eu PL - no irradiation
GaN:Eu PL - irradiated
GaN:Eu alpha-induced luminescence
450
500
550
600
650
Wavelength (nm)

Fig. 2


Normalized Luminescence Intensity (AU)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10^{12}
10^{13}
10^{14}
10^{15}
Fluence (ions/cm^2)
5.5×10^{10} ions/sec/cm^2
2.8×10^{11} ions/sec/cm^2
1.4×10^{12} ions/sec/cm^2
Model with defect creation only
Model with defect creation and luminescent center destruction